Studies of the Rare-Earth Hydrides

Technical Report III

# PRESSURE-TEMPERATURE-COMPOSITION STUDIES OF THE LANTHANUM-, CERIUM-, PRASEODYMIUM-, NEODYMIUM-, SAMARIUM-, and YTTERBIUM-HYDROGEN SYSTEMS. EXPERIMENTAL

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## Experimental

### Introduction

Studies of the pressure-temperature-composition relationships for the various rare earth metal-hydrogen systems comprised a major line of investigation of these systems. Such an investigation demands the use of a vacuum line, with suitable methods of measuring pressure, temperature, and composition. Methods of measurement will be described briefly here, and a more complete description of the apparatus constructed for use will be found in the following sections of this chapter.

Pressure measurements were made using a mercury manometer, a cathetometer, or a McLeod gauge, depending on the magnitude of the pressure to be measured.

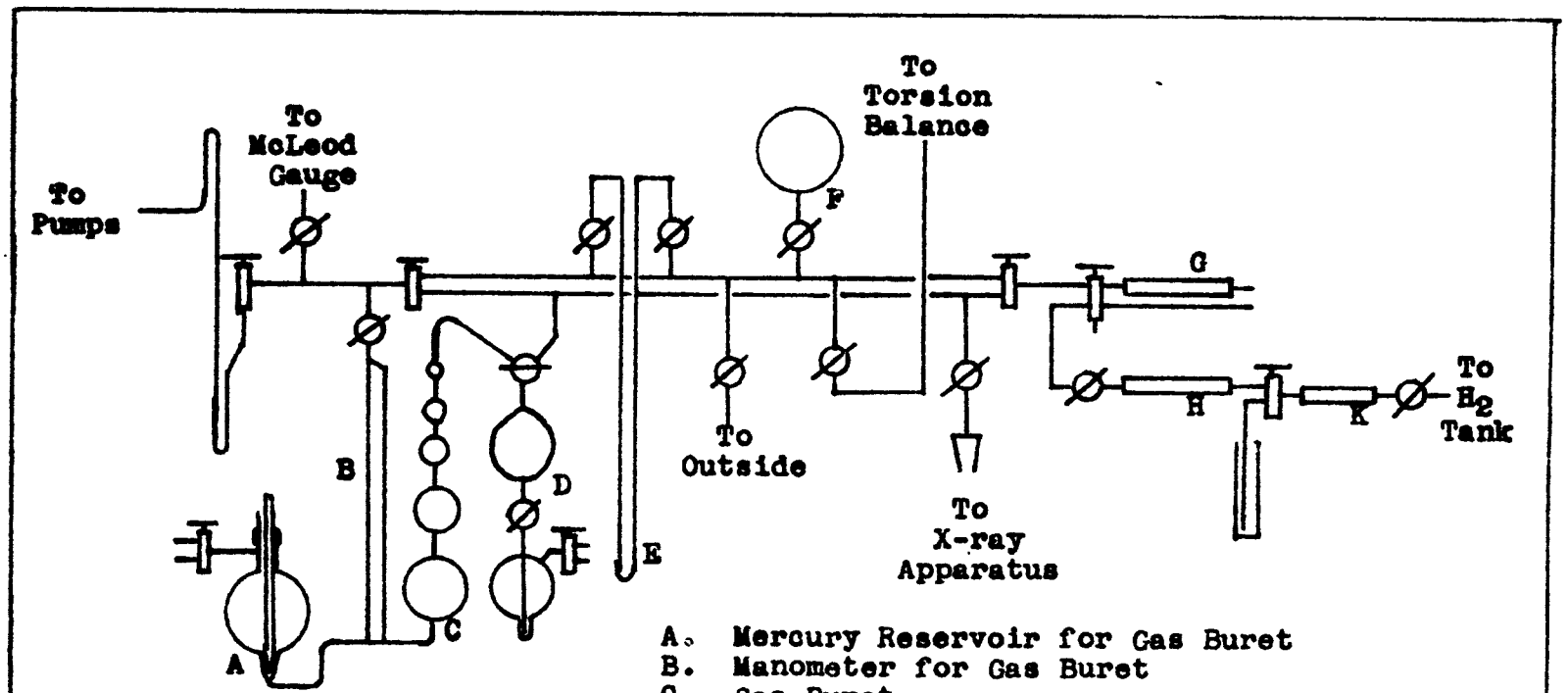
A high-temperature thermostatted furnace was used to maintain temperatures, which were measured with thermocouples.

A silica torsion balance was constructed for use in determining the composition of the solid phase present. In a few experiments a silica helix balance was used.

Apparatus

Vacuum line.--A schematic diagram of the vacuum line constructed for use in these investigations is shown in Figure 1. It may be seen from the diagram that the line consisted essentially of two different sections, one of which was used in preparing the samples for X-ray diffraction studies, and the other for dissociation pressure measurements.

The former included a Toepler pump and gas buret, and a ground-glass joint for attaching the apparatus with the capillaries sealed to it. A detailed description of this apparatus is given in Chapter V. The other section of the line included a mercury manometer, a 1-liter storage bulb, a connection to the torsion balance, and an opening, via stopcock, to the outside, for use in glass-blowing or in admitting nitrogen to the line. Either section could be evacuated with a mercury diffusion pump and fore-pump. Both sections used the same McLeod gauge, and were also connected to the same uranium hydride reservoir used for purifying the hydrogen. For experiments using deuterium, a uranium deuteride reservoir was sealed directly to the line.




A. Mercury Reservoir for Gas Buret
B. Manometer for Gas Buret
C. Gas Buret
D. Toepler Pump
E. Manometer
F. 1-Liter Gas Storage Bulb
G. Uranium Hydride Reservoir
H. "Anhydrone" Drying Tube
J. Mercury Bubbler
K. "Deoxo" Catalyst

Figure 1. Schematic Diagram of Vacuum Line

Manometer.--The manometer was constructed of 13-mm. tubing, and both arms were connected through stopcocks to the manifold. Readings were made to the nearest estimated 0.1 mm. in each arm. A glass scale was used, and temperature corrections applied when justified (International Critical Tables, I, 68-69). The resulting values were rounded off to the nearest millimeter.

Cathetometer.--The cathetometer used was actually a small travelling microscope which had been converted to a telescope by use of a different objective lens. It was read to 0.01 mm. for each arm of the manometer. Temperature correction for a brass scale was applied, and resulting pressure values were rounded off to the nearest 0.1 mm., unless the pressure being read was in the plateau region discussed below. The cathetometer was used for the pressure range of 3 to 40 mm.

McLeod gauge.--The McLeod gauge used was similar to that described by Strong (1938). Calibration and operation of the gauge were also essentially the same as described there. The principal point of difference worth noting is that there was a small bulb blown in the lower end of the capillary atop the large bulb $V_1$, giving a value of $\Delta h_0$ of 2.00 cc. The equations for the low and high pressure ranges were:

1) $P = 4.10 \times 10^{-6}(\Delta h_{mm})^2$ mm., corresponding to (14) of Strong, and

2) $P = 0.01(\Delta h_{mm})$ mm., corresponding to (15) of Strong.

The largest value of $\Delta h_{mm}$ possible in 1) was about 125 mm., corresponding to a pressure of about 0.064 mm., and the largest value of $\Delta h_{mm}$ possible in 2) was 310 mm., corresponding to a pressure of 3.1 mm. Readings for equation 2) were too low by 1% because of pressure in the capillary, and they were too high by about 0.5% because of the temperature factor. The net effect of about 0.5% error due to these factors was neglected, since readings were taken to the nearest mm., unless the value of $\Delta h$ was of the order of 10 mm., in which case an effort was made to obtain a more careful reading.

Readings for equation 1) were also taken to the nearest mm., and since the lowest pressures measured were usually above 0.01 mm., corresponding to $\Delta h$ of approximately 50 mm., an error of about 2% was possible here.

Gas buret.--The gas buret consisted of five bulbs, and was connected at its upper end to a Toepler pump of the usual design of 150-cc. capacity, and at its lower end to a mercury reservoir and to vertical lengths of tubing of the

sizes connecting the bulbs, so that pressures could be ascertained.

Torsion Balance.--See Technical Report II

Helix balance.--In a few of the experiments in which smaller metal samples were used, especially with the metals ytterbium and samarium, a silica helix balance was used, of the usual design. Its total capacity was approximately 300 mg. Extension of the helix with respect to a fiducial pointer was measured with a filar micrometer microscope. Sensitivity of the set-up used was 0.36 mg./scale division. This balance was used only for deuteride preparations, in which the maximum increase in weight of a 200-mg. sample would be 6 to 8 mg. Since 0.01 scale division could be read, high accuracy in measuring composition appears possible of being attained, but this was to a large extent nullified by irreproducibility of the readings, owing principally to vibration. Accuracy of composition measurements is estimated to be within 1%, however.

High-temperature thermostatted furnace.--See Technical Report II.

Thermocouples.--Temperatures were measured using Chromel-Alumel thermocouples, constructed of No. 20 wire (0.81 mm.) and checked against standard melting-point samples of zinc (419.43° C.) and aluminum (659.7° C.) obtained from the National Bureau of Standards. As first prepared, these thermocouples showed a deviation from the standard samples of less than 0.2° C. (<0.01 millivolt). With prolonged use, however, the thermocouples began to read high, and corrections amounting to as much as 2° C. had to be applied. Standard conversion tables "Standard 31031" published by the Leeds & Northrup Company were used.

The thermocouple wires adjacent to the junctions were threaded through twin-bore porcelain insulators, which were then inserted into lengths of 7-mm. vycor tubing. This tubing, in the case of the hot junction, was fastened to the long silica tube extending down into the furnace, so that the junction was at the same level as the sample inside the molybdenum-foil cup. The cold junction was maintained at 0° C. in an ice-water mixture in a Dewar flask.

Potentiometer.--Thermocouple voltages were measured using a Leeds & Northrup Portable Precision Potentiometer

Model No. 8662. In the temperature range of the experiments the corresponding voltages extended from approximately 22 to 35 millivolts, and the instrument could be read to the nearest 0.01 millivolt, equivalent to approximately 0.24° C. The standard cell in the instrument was occasionally checked against Eppley standard cells which had been compared to N. B. S. cells.

## Reagents

Preparation of the metal samples.--The metals lanthanum, cerium, praseodymium, neodymium, samarium, and ytterbium were obtained through the courtesy of Dr. F. H. Spedding of the Institute for Atomic Research, Iowa State College, Ames, Iowa. The preparation of the first four of these metals by reduction of the rare earth chloride with calcium is described by Spedding & Daane (1952). These metals were described by Dr. Spedding[1] as containing the following possible impurities, below the limits indicated:

<150 ppm Ca in each metal;

<500 ppm Ce, Pr, and Nd in the La;

<500 ppm Nd and La in the Ce and Pr;

<600 ppm Sm in the Nd;

a few ppm Fe and Mg, and some dissolved nitride and

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[1]Spedding, F. H. Private communication, 1951.

oxide (perhaps 0.1 to 0.2% oxide) in each metal. The preparation of samarium and ytterbium by reduction of the oxides with lanthanum, and simultaneous volatilization, has been described by Laane, Dennison & Spedding (1953). Spectrographic analyses were supplied and gave the following data:

Samarium: <0.01% Ca, Mg, Fe;
<0.05% Nd, and Gd;
~0.25% Eu;
La, Si, Ta not detected.

Ytterbium: <0.01% Al, Ca, Na;
Fe, La, Lu, Ta, Tm not detected.

Europium metal was prepared by the same method through the courtesy of Dr. Spedding from europium oxalate decahydrate graciously loaned by Mrs. Herbert N. McCoy. The metal contained <150 ppm La or Ca, with Gd, Sm, Fe, Cu, Ta, and Si not detected.[1]

The metals lanthanum, cerium, praseodymium, and neodymium were received under mineral oil, and stored in this way. A recent communication from Dr. Spedding stated his belief that this is poor practice, and that the rare earth metals slowly react with the oil to form hydrides and carbides in the metal.[2] He also stated that metal which has been stored under oil evolves considerable gas, most of which is hydrogen. A weight decrease of the order of 1 mg.,

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[1,2]Spedding, F. H. Private communication, 1955.

possibly owing to loss of hydrogen, was observed a number of times in this investigation when samples of metal weighing approximately 750 mg. had been heated to 600° C. in a vacuum.

Samples of these metals were prepared by first cutting the large massive block into smaller pieces of slightly more than the desired weight with a glass-cutting wheel; simultaneous cooling by a stream of water was essential. Individual samples were cleaned with a file under mineral oil, rinsed in light petroleum ether (Skelly A), and subsequently kept under this liquid until they were placed in the pan of the torsion balance, except for time spent in weighing them. This procedure of cleaning, weighing, placing on the balance, and subsequent evacuation of the system was always carried out as rapidly as possible.

Ytterbium and samarium were merely kept stored in small, tightly-closed containers, since they react very slowly with air. Samples were prepared as described above, except that they were not cleaned under mineral oil, and were cut initially with a chisel.

Europium metal is much more reactive than any of the rare earth metals mentioned above. It was kept sealed in glass under vacuum, and samples used were made up of shavings cut off with a knife, in a dry box filled with $CO_2$.

Purification of hydrogen.--Tank hydrogen was passed first through a "Leoxo" platinized asbestos catalyst, to convert the oxygen impurity to water, and then through a drying tube containing "Anhydrone" (magnesium perchlorate). It was then passed through a uranium hydride reservoir, which was maintained at a temperature of approximately 750° C. If only a small quantity of hydrogen was desired, it was sometimes obtained by merely heating the reservoir, to evolve the desired amount (Spedding, Newton, Warf, Johnson, Nottorf, Johns & Laane, 1949). Sturdy & Mulford (1956) mention that mass spectrometer analysis of hydrogen obtained from the thermal decomposition of uranium hydride has shown the major impurity to be 0.02% nitrogen.

Deuterium was obtained from a reservoir of uranium deuteride, which had been prepared from massive uranium and tank deuterium. The latter was obtained from the Stewart Oxygen Company, and was labelled as 99.5% deuterium. The molecular weight of the gas, assuming 0.5% hydrogen, was calculated as (0.995 x 2.0147) + (0.005 x 1.0081) = 2.01.

Procedure in preparing hydrides

The following paragraphs describing hydride preparations apply to preparations on the torsion and helix balances, and in the X-ray capillary apparatus, described in

Chapter V. As a rule the metal samples, prepared as described in the preceding section, were outgassed for several hours at 600° C., and then cooled to room temperature before hydrogen was admitted to the system. Reaction usually occurred in a few minutes after this preliminary treatment.

Metal samples which had not undergone this preliminary treatment did not usually react with hydrogen until they had been heated to a temperature which varied over a range of 260-365° C., at least for a number of lanthanum and cerium samples. However, on a few occasions reaction did occur at room temperature even without any preliminary heating or outgassing of the sample. On a few occasions hydrogen was admitted to metal samples which were being maintained at a temperature of approximately 300° C.; reaction was usually immediate under such circumstances.

Some plots showing the quantity of hydrogen absorbed with time are given in Appendix I, Figures 9-12. These are all for samples of metal which had not previously been treated with hydrogen.

In an effort to obtain maximum absorption, the reaction, once it had begun, was usually allowed to continue at room temperature. Results were not very concordant, as absorption usually occurred to a hydrogen:metal atomic ratio of from approximately 2.6 to 2.9. On one occasion

absorption to 2.96 was measured volumetrically for a sample of lanthanum hydride prepared in the X-ray capillary apparatus. If the hydride samples were taken through additional heating and cooling cycles, in which hydrogen would be evolved and re-absorbed, and again allowed to cool to room temperature in hydrogen, additional absorption often occurred, to a somewhat higher hydrogen-metal atomic ratio.

This additional absorption on longer treatment is interpreted as a sign that initially the entire metal sample had not reacted with hydrogen. Such behavior provided the largest contribution to the error in the measurement of the composition of the product. This matter has already been mentioned above in connection with the report of Muthmann & Baur (1902). It is believed that such incomplete reaction may be due to an oxide layer on the grains of the massive metal sample. Similarly, the initial lack of reactivity of most metal samples which had not undergone any preliminary heating and outgassing may also be due to the presence of oxides.

Measurement of dissociation pressures

As a rule, dissociation pressure curves were obtained isothermally--that is, the temperature was maintained at a constant value, and hydrogen was added to the system or removed from it. Once equilibrium had been reached, the

pressure was measured, and the composition was determined from the reading obtained with the torsion balance (or the helix balance). Actually, a number of readings were often taken, until it was seen that the system was not undergoing further change. Equilibrium was usually established quite rapidly, however, and as a rule measurements of different points were made 10 to 15 minutes apart.

Most of the dissociation pressure data were obtained both by desorption and absorption of hydrogen by the sample. This is to say that an isotherm at a given temperature was usually first constructed from a series of points obtained by evolution of hydrogen from the sample. A corresponding isotherm was then constructed from a series of points obtained by re-absorption of hydrogen by the sample. Such pairs of isotherms usually showed good agreement, well within experimental error. In plots of the data, only a single isotherm has therefore been drawn through all points obtained at a given temperature. The dissociation pressure data obtained for the various metal-hydrogen systems are given in Appendix II, Tables 7-18, and are shown graphically in Appendix II, Figures 13-25.[1]

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[1] Two graphs are presented for each system: one for the plateau-pressure region and lower pressures at very low compositions in the few instances in which these latter points were obtained, and the second graph for the high-pressure region.

The isotherms for the systems formed by hydrogen and the metals lanthanum, cerium, praseodymium, and neodymium[1] displayed in general the behavior first described in detail by Sieverts & Muller-Goldegg (1923) for mischmetal-hydrogen systems at 800° C.; that is, they consisted of three different branches. These are: 1) an initial ascending curve at low hydrogen composition, 2) a constant-pressure plateau indicating the co-existence of two solid phases, and 3) a final ascending curve extending into the region of higher hydrogen composition.

The exact limits of the two-phase region were not very precisely determined in most cases, but it was apparent that they were dependent on the temperature and the particular metal. In general, however, these limits were near the compositions $MH_{0.4}$ and $MH_{1.8}$, approaching each other as the temperature was raised, and thus indicating that above a certain "critical" temperature the horizontal portion of the isotherms would disappear.[2] This disappearance was observed by Sieverts & Roell (1925) for isotherms at 1100° C. However, as the authors reported, samples which

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[1]The samarium-hydrogen system is discussed in Appendix IV.

[2]Actually, the 800° C. isotherms, as determined by Sieverts & Muller-Goldegg and also for some systems in the present investigation, already display a slight slope in the plateau pressure region.

had been pumped on at this temperature melted, though hydrogen-rich samples did not. The isotherms gave no indication of the formation of the liquid phase. It was not established that a sample which had been melted in this manner would still absorb hydrogen, and display a plateau in the dissociation pressure isotherm at 800° C. Other complications here would be possible reaction with the container, and vaporization of the rare earth metal. This would be an interesting region for further investigations.

The limits of the two-phase region found at 800° C. by Sieverts & Muller-Goldegg were near the compositions $MH_{0.2}$ and $MH_{1.5}$. Maximum absorptions in most of their experiments went only to compositions of $MH_{2.7}$, however, compared to $MH_{2.9}$ in the present investigation, as discussed below.

The dissociation pressure values reported by Sieverts & Muller-Goldegg for the two-phase region of the 800° C. isotherms are approximately the same as those determined in the present investigation. Zhukov (1913) had earlier reported that the dissociation pressure between 450° and 510° C. for cerium hydride was about 1 mm. as long as the proportion of hydrogen did not exceed that corresponding to $CeH_2$, but this is very high compared to the pressure of approximately 0.02 mm. found for the cerium-hydrogen system

at the considerably higher temperature of 598° C. in the present investigation.

Isotherms reported by Mulford & Holley (1955) for the cerium-, praseodymium-, and neodymium-hydrogen systems are very similar to those reported in this dissertation. No very significant differences exist. One point of difference is the location of part 3) of the isotherms with respect to the composition axis. Reference may be made here to the preceding section on preparation of the hydrides, in which there is given a short discussion concerning the often-observed initial incomplete reaction of the entire metal sample with hydrogen. It was found that even after a number of heating and cooling cycles, and subsequent measurement of a series of points at each of a number of different temperatures, sudden additional absorption would occur. Subsequent re-determination of the isotherms would show them to be shifted to the right along the composition axis, toward higher compositions. Often later experiments, carried out in an effort to determine the reproducibility of earlier results, showed a similar displacement of the isotherms. Many of the results were discarded because of this effect, and those remaining, at least in the region of the third, or ascending branch of the isotherms, were usually derived from experiments in which the maximum absorption

had reached a composition of approximately $MH_{2.9}$, after several cycles of heating and cooling.

Plateau pressures, which Mulford & Holley also reported for the lanthanum-hydrogen system, are not too widely different, except in the case of cerium. A more detailed comparison is given below.

# APPENDIX I

## RATE OF ABSORPTION DATA

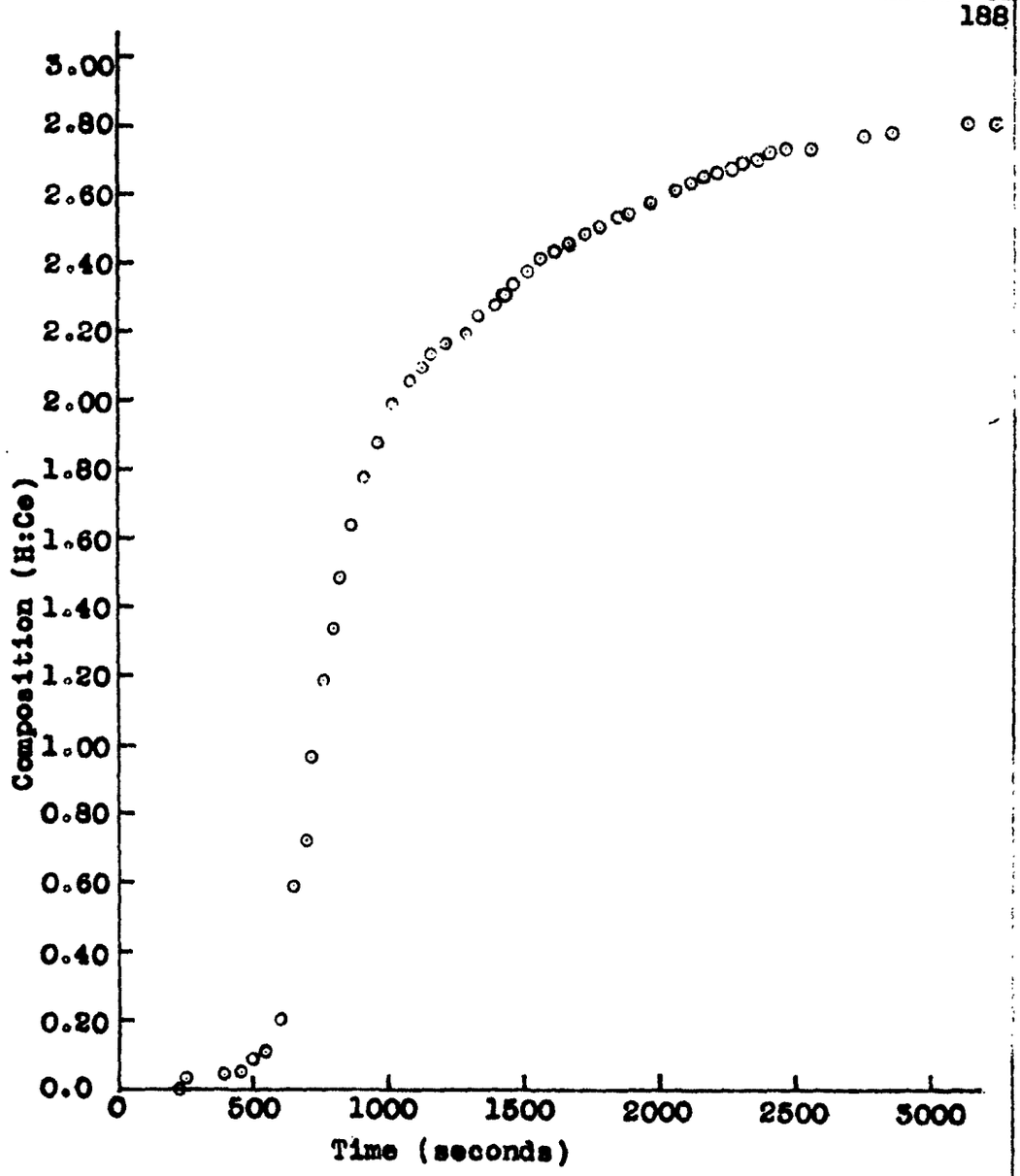


Figure 9.

Rate of absorption of hydrogen by cerium.
Temperature ~60° C., Pressure ~770 mm.
Experiment 7-218.

Sample had been outgassed at 600° C.

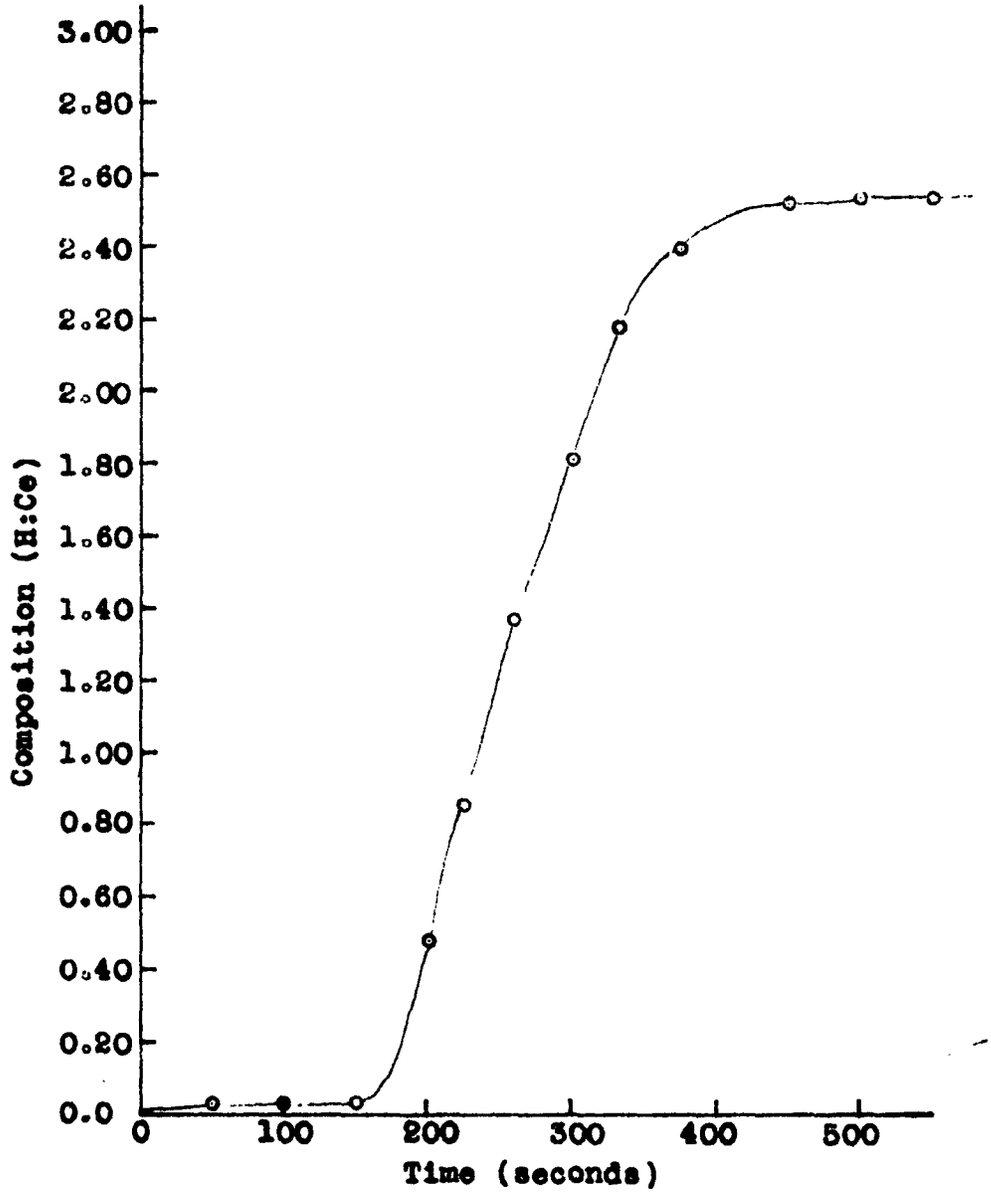


Figure 10.

Rate of absorption of hydrogen by cerium.
Temperature ~350° C., Pressure ~600 mm.
Experiment 7-237.

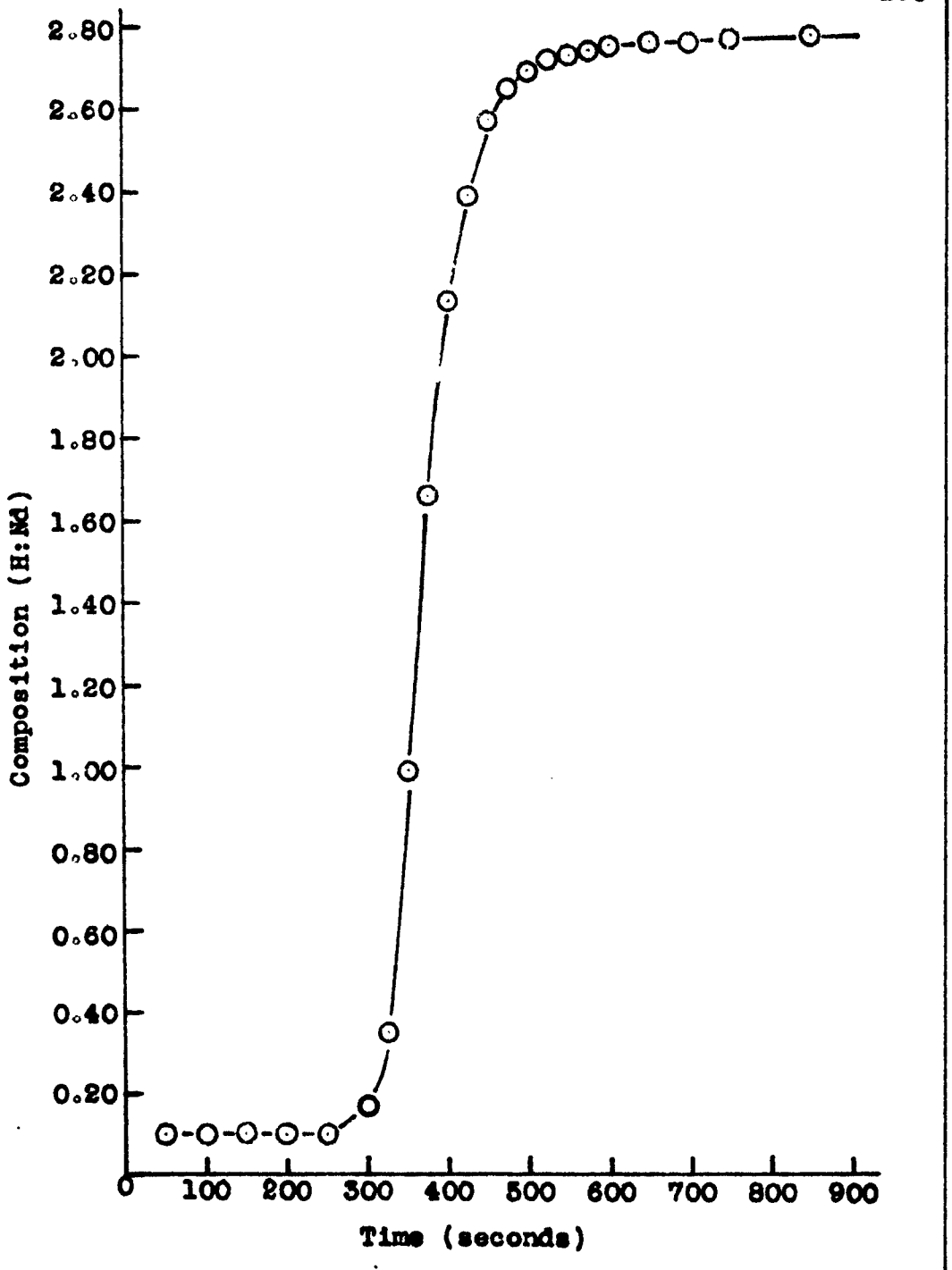


Figure 11.

Rate of absorption of hydrogen by neodymium. Temperature ~29° C., pressure ~680 mm. Experiment 7-255.

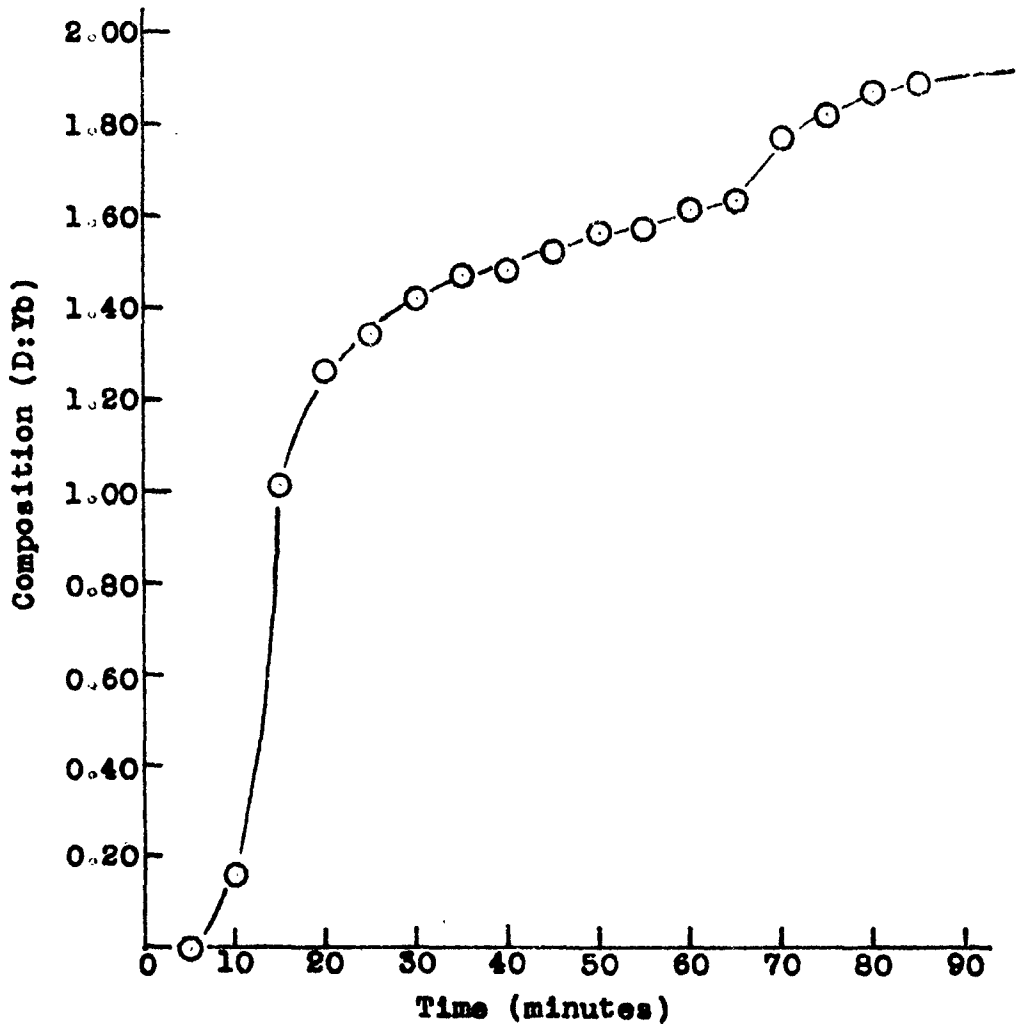


Figure 12.

Rate of absorption of deuterium by ytterbium. Temperature 400° C., initial pressure 450 mm., final pressure 350 mm. Temperature had increased slightly at 65-minute mark, increasing rate for a time. Data from Experiment 6-219. The metal had been exposed to deuterium about 20 hours at room temperature, and then was heated over the course of 55 minutes to 400° C., at which point the graph above begins. Maximum absorption went to $YbD_{1.93}$

See Technical Report I for references